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## EUROPEAN PATENT APPLICATION

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**(54) Diamond-like carbon coatings.**

**(57) A method for depositing a diamond-like coating upon a substrate, including the operations of depositing upon a substrate material a foundation layer of a material known to be conducive to the formation of diamond-like carbon as hereinbefore described, and then depositing a layer of diamond-like carbon upon the foundation layer.**

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The present invention relates to the deposition of hard carbon coatings and in particular those which have a structure similar to that of diamond.

Because of their potential for high wear resistance, low coefficient of friction and chemical virtues, hard and coherent layers of carbon are being investigated for a variety of tribological applications. Ideally, the coatings should be of diamond, but it has proved difficult to deposit continuous crystalline diamond layers with good adherence upon certain technologically important substrate materials. These difficult materials include steels, nickel alloys, cobalt cemented tungsten carbide and most substances containing transition metal elements. Substrate materials favourable for the deposition of diamond include diamond itself, silicon, silicon carbide and other materials in which it is believed that conditions are present which enable hetero-epitaxy to occur.

An alternative to the deposition of diamond is the deposition of so-called diamond-like carbon coatings. Diamond-like carbon is distinct from both diamond and graphite. It is amorphous and is characterised by having planar  $Sp_3$  interatomic bonding (as in graphite) rather than  $Sp_2$  bonding (as in diamond) but it has a hardness approaching that of diamond. The mechanical, optical and other characteristics of diamond-like carbon stem from its amorphous nature and the absence of graphitic microcrystallites.

A method of depositing carbon by an ion-assisted process has been described previously in United Kingdom patent specification 2,122,224. In this process a source of hydrocarbon vapour is placed in a vacuum chamber near to work-pieces that simultaneously are bombarded with energetic ions, for example, nitrogen ions. The ion bombardment causes the decomposition of hydrocarbon molecules on the surface of the work-pieces to provide a coating of hard and adherent carbon.

However, this procedure does not always produce amorphous diamond-like carbon. By means of laser Raman spectroscopy it has been shown that this is so only on favourable substrate materials such as silicon, alumina, silicon nitride and other ceramics. In the case of steel, nickel, germanium and other similar materials it appears that the growth of graphitic microcrystals occurs and this is correlated with the formation of a soft coating with poor tribological properties.

The present invention provides a method by means of which hard diamond-like carbon coatings can be deposited in a wide range of substrates including those at present known to be unfavourable for the deposition of such coatings.

According to the present invention there is provided a method for depositing a diamond-like carbon coating upon a substrate, including the operations of depositing upon a substrate material a foundation layer of a material known to be conducive to the for-

mation of diamond-like carbon as hereinbefore defined, and then depositing a layer of diamond-like carbon upon the foundation layer.

Suitable materials for the foundation layer are silicon nitride, silicon, alumina, and boron nitride.

Preferably, both the foundation layer and the layer of diamond-like carbon are deposited by means of an ion-assisted process.

The invention will now be described, by way of example, with reference to the accompanying diagrammatic drawing of an apparatus suitable for the performance of the invention.

Referring to the drawing, a vacuum chamber 1 includes a rotatable support 2 for a number of work-pieces 3, an electron beam heated hearth 4, an ion beam source 5 and a nozzle 6 through which hydrocarbon vapour can be directed at the workpieces 3.

In use, the workpieces 3 to be coated are placed on the support 2, a piece of a suitable material 7 for forming the foundation layer is placed upon the hearth 4 and the vacuum chamber 1 is closed and evacuated to a pressure of some  $10^{-6}$  Torr. Suitable materials are silicon, aluminium or boron. The electron beam to heat the hearth 4 is then switched on together with the ion beam source 5, which is such as to provide the ions (for example oxygen or nitrogen) which are required to form the desired material for the foundation layer. Suitable ion energies are in the range 40-80 KeV. The rates of arrival of coating atoms and ions at the workpieces 2 are adjusted to produce a coating of the required material upon the surface of the work-pieces 3. When sufficient material has been deposited to form a complete foundation layer the ion beam hearth 4 is switched off, but the ion beam source 5 is kept running. A stream of hydrocarbon vapour is then directed at the workpieces 3 from the nozzle 6 while the surface of the workpieces 3 are bombarded with ions having an energy in the range 40-80 KeV and a beam current density of some  $5 \mu A cm^{-2}$  for a period of some 4 hours during which time the pressure in the vacuum chamber 1 is maintained at about  $10^{-6}$  Torr.

A suitable source for the hydrocarbon vapour is a quantity of polyphenyl ether 8 which is contained in a heated vessel 9 out of which the nozzle 6 leads.

If desired, the ion beam source 5 may be energised before the electron beam hearth 4 so as to enable the surfaces of the workpieces 3 to be cleaned by sputtering before the deposition of the foundation layer is begun.

The apparatus as described has a twin-anode ion source but other types of ion source such as that known as a bucket ion source can be used.

## 55 Claims

1. A method for depositing a diamond-like carbon coating upon a substrate, including the oper-

ations of depositing upon a substrate material a foundation layer of a material known to be conducive to the formation of diamond-like carbon as hereinbefore defined, and then depositing a layer of diamond-like carbon upon the foundation layer.

2. A method according to claim 1 wherein the foundation layer comprises a layer of silicon, silicon nitride, boron nitride, or alumina.

3. A method according to claim 1 or claim 2 wherein both the foundation layer and the layer of diamond-like carbon are deposited by means of an ion assisted process.

4. A method according to claim 3 wherein there is included the operations of placing in a vacuum chamber (1) a substrate (3) upon which there is to be formed a foundation layer prior to the deposition on the substrate (3) of a layer of diamond-like carbon, producing in the region of the surface of the said substrate (3) a population of atoms of a first species to be used to form the foundation layer, irradiating the surface of the substrate (3) with ions of a second species so as to cause the atoms of the first species to form an adherent foundation layer on the surface of the substrate (3), providing a carbon containing species in the region of the surface of the substrate and subjecting the substrate to further irradiation with the ions of the second species thereby to cause carbon atoms to be deposited upon the surface of the foundation layer as a diamond-like coating as hereinbefore defined.

5. A method according to claim 4 wherein the ions of the second species are capable of reacting with those of the first species to form the foundation layer.

6. A method according to claim 5 wherein the population density of the first and second species at the surface of the substrate (3) is such as to cause the desired material for the foundation layer to be formed and deposited upon the surface of the substrate (3).

7. A method according to claim 5 or claim 6 wherein the first species is silicon, aluminium or boron and the second species is oxygen or nitrogen.

8. A method according to any of claims 4 to 6 wherein the carbon containing species is an hydrocarbon vapour.

9. A method according to claim 8 wherein the carbon containing species is polyphenyl ether.

10. A method according to any of claims 4 to 9 wherein the ions are nitrogen ions having an energy in the region of 100 KeV and are in the form of a beam having a current density in the region of 5  $\mu$  A cm<sup>-2</sup>.

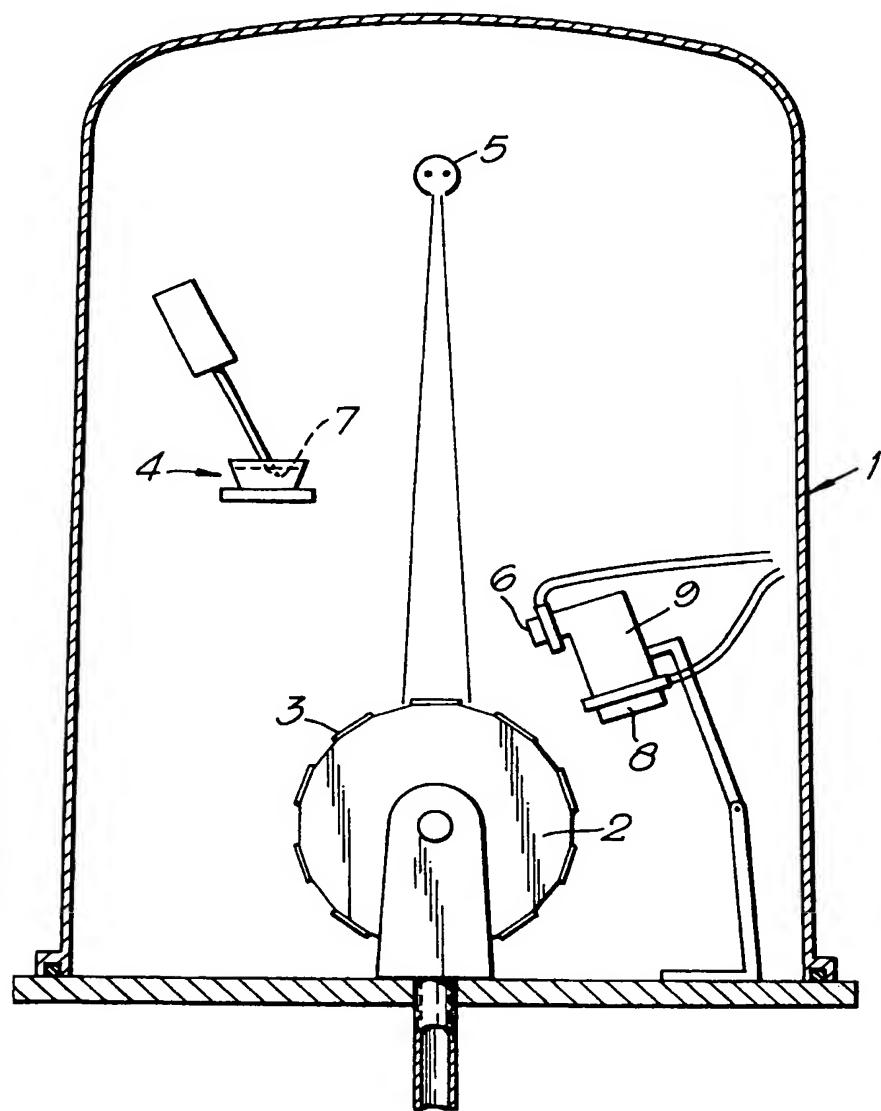
11. A method according to any preceding claim wherein the surface of the substrate is bombarded with the ions of the second species prior to the formation of the foundation layer so as to clean the surface of the substrate.

12. An apparatus for depositing a diamond-like coating upon a substrate, wherein there is provided a vacuum chamber (1) encompassing a support (2) for a substrate (3) upon which there is to be deposited a coating of diamond-like carbon, as hereinbefore defined, a source (4, 7) of atoms of a first species adapted to form a foundation layer upon a substrate, a source (5) of ions of a second species and a source (6, 8, 9) of a carbon containing species.

13. An apparatus according to claim 12 wherein the source of atoms of the first species is a hearth (4) upon which the said material can be heated to a temperature at which it has a significant vapour pressure.

14. An apparatus according to claim 11, claim 12 or claim 13 wherein the source of (6, 8, 9) of a carbon containing species is a source of hydrocarbon vapour.

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## EUROPEAN SEARCH REPORT

Application Number

EP 91 30 7279

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.5)								
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim									
X	EP-A-0 372 696 (SEMICONDUCTOR ENERGY LABORATORY) * claims 1,2,8 * -----	1-3	C23C16/26 C23C16/02 C23C14/06								
X	EP-A-0 259 791 (KERNFORSCHUNGSAVLAGE JULICH) * column 1, line 33 - line 38; claims 1,2 * -----	1-3									
A	US-A-4 656 052 (SATOU ET AL.) * claim 1 * -----	4-14									
A,0	GB-A-2 122 224 (UNITED KINGDOM ATOMIC ENERGY AUTHORITY) * page 2, column 1, line 1 - line 7; claims 1-9 * -----	4-14									
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)								
			C23C C30B								
<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>18 DECEMBER 1991</td> <td>PATTERSON A. M.</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	18 DECEMBER 1991	PATTERSON A. M.		
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<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td colspan="2" style="width: 50%;">CATEGORY OF CITED DOCUMENTS</td> <td colspan="2" style="width: 50%; text-align: right;">T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</td> </tr> <tr> <td colspan="2"> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document </td> <td colspan="2"></td> </tr> </table>				CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document		X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
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